I and shown graphically as a function of ΔG_{Co} in Figure 3. The absence of any significant broadening of the center member of the triplet phosphorus resonance throughout the series of compounds suggests that virtual equivalence of the two three-bond coupling constants is maintained throughout the series. In order to avoid extensive protonation of the phosphodiester moiety (p*K* = –0.04[2]) and the possible attendant effects on H–P coupling constants, the base-off cobalamins were observed at pHs above about 0.8 and the observed coupling constants corrected for the presence of the base-on species by eq 5, where $J_{\text{H-P}}^{\text{obsd}}$ is the

$$J_{\text{H-P}}^{\text{base-off}} = (J_{\text{H-P}}^{\text{obsd}} - \alpha_{\text{base-on}} J_{\text{H-P}}^{\text{base-on}})/(1 - \alpha_{\text{base-on}}) \qquad (5)$$

observed coupling constant at the measured pH and $\alpha_{\text{base-on}}$ is the fraction of base-on species present at that pH. This correction was not significant (to two significant figures) for any compound (Table I). The resulting values show that all of the base-off cobalamins have the same H–P coupling constant (7.3 ± 0.1 Hz), strongly supporting our contention[2] that the conformation of the phosphodiester is identical for all the base-off species. The base-on cobalamins, however, show a steady, and apparently linear increase in $J_{\text{H-P}}$ with increasing strength of coordination (Figure 3), although the range of values is quite small. This suggests a steady but small change in H–C–O–P dihedral angle as the axial Co–N bond length is changed, accompanying the small changes in CO–P–OC bond angles, which are responsible for the previously described ^{31}P chemical shift trends.[2] Most interestingly, the coupling constants are identical for the base-on and base-off species of two of the cobalamins (CH_3Cbl and CF_3CH_2Cbl), as was also the case for the ^{31}P chemical shifts of the base-on and base-off species of these two compounds.[2] This supports our contention that when the axial benzimidazole is bound moderately weakly and the axial Co–N bond length is about 2.19 Å (as it is in base-on CH_3Cbl[10]), the nucleotide loop is not strained (relative to the base-off species) and the phosphodiester conformation is the same in both the base-on and base-off species. However, when the axial Co–N bond length is either increased (as in AdoCbl, 2.24 Å[9]) or decreased (as in "wet" CNCbl, 1.97 Å[8]), the nucleotide loop is strained and the phosphodiester conformation is changed, leading to the observed changes in phosphorus chemical shift and H–P coupling constants.

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Synthesis and X-ray Crystal Structure of (Dicyanodihydroborato)bis(triphenylphosphine)copper(I): A New Linear Polymer

Sir:

There has been considerable interest in the various modes of coordination shown by the BH_4^- and BH_3CN^- groups,[1] and, following the recent synthesis of $BH_2(CN)_2^-$,[2] its role as a ligand is being explored. The first reported complexes of this species [$(Ph_2MeP)_3Cu(NC)_2BH_2$ and $P^3Cu(NC)_2BH_2$ (P^3 = 1,1,1-tris((diphenylphosphino)methyl)ethane)][3] contain only one cyano group coordinated to Cu(I) in monomeric compounds. This communication reports that in the related compound of empirical formula $(PPh_3)_2Cu(NC)_2BH_2$, *both* CN groups are coordinated to *different* copper(I) atoms. The result is that the molecule exists as a linear polymer of an unprecedented type in cyanohydroborate complexes. The polymer is obtained from reactions between equimolar quantities of $Na(NC)_2BH_2{\cdot}0.65(\text{dioxane})$ and either $(PPh_3)_3CuCl$ or $(PPh_3)_2CuCl$, with the colorless product being recrystallized from hot CH_3CN. Anal. Calcd: C, 69.89; H, 4.95; N, 4.29. Found: C, 69.59; H, 4.94; N, 4.35. The complex is insoluble in CH_2Cl_2, $CHCl_3$, C_2H_5OH, CH_3OH, C_6H_6, tetrahydrofuran, and dimethylformamide. Mp: 244–250 °C. Crystal data: $C_{38}H_{32}BCuN_2P_2$; M_r = 652.98; triclinic; space group $P\bar{1}$; a = 13.708 (3), b = 20.179 (4), c = 13.369 (3) Å; α = 105.81 (2), β = 100.16 (2), γ = 102.04 (2)°; V = 3371 (1) Å^3; Z = 4; D_{calcd} = 1.29 g cm^{-3}; μ(Mo Kα) = 0.798 mm^{-1}. Diffraction data obtained by using ω scan [$2\theta < 55°$] techniques were collected at 24 °c on a Rigaku Automated four-circle diffractometer, Type AFC-5A, using graphite-monochromated molybdenum radiation (Mo Kα (0.71073 Å). Parallelepiped-shaped crystals were used of dimensions 0.40 × 0.35 × 0.20 mm^3. A total of 15 180 reflections ($\pm h,\pm k,+l$) were collected. The structure was solved by using the heavy-atom method with all hydrogen atom positions determined by difference Fourier synthesis. Scattering factors and anomalous scattering factors for non-hydrogen atoms[4,5] and scattering factors for hydrogen atoms[6] were taken from known references. A local version of the UNICS program system was used for analysis.[7] Final R value was 0.047 for 8392 reflections with $|F_o| > 3\sigma(F_o)$. No estimate of agreement between equivalent reflections was made, nor were corrections made for absorption.

The crystal structure reveals the polymeric nature of the compound (Figure 1). The complex exists as a polymer parallel to the c axis of the unit cell with the copper atoms bridged by $(NC)_2BH_2^-$. The chains are sufficiently far apart such that only interactions of the van der Waals type can occur between them. Although there are two crystallographically independent units in the polymer chain, their configurations are almost the same. Each copper atom is surrounded by two phosphorus and two nitrogen atoms in a slightly distorted tetrahedral arrangement.

The IR spectrum of the complex (Nujol mull) in the CN region contains two strong absorptions at 2223 and 2206 cm^{-1}, both higher than that of the free ligand (2203 cm^{-1}), indicating that both CN's are bound to the metal. (In the related $MePh_2P$ and P^3 complexes containing both free and coordinated CN groups, absorptions are observed at frequencies higher *and* lower than those of the free ligand.)[3] There are typical absorptions in the B–H region: 2418 (m–w), 2400 (s), 2385 (s), 2370 (m) cm^{-1}.

The ^{11}B NMR spectrum consists of a 1:2:1 triplet, (δ = –42.3 referenced to $BF_3{\cdot}OEt_2$, J = 95.3 Hz), indicating that the boron signal is split by two equivalent hydrogens. The center of the multiplet is shifted only slightly from that of the free ligand (–42.1 ppm, CH_3CN) indicating little pertubation of the electron density on the boron nucleus upon coordination of the nitrogen to the metal.

Preliminary results indicate that this type of polymer may not be unique to PPh_3. Compounds of empirical formulas $(Ph_2PCH_2CH_2PPh_2)Cu(NC)_2BH_2$ and $(MePh_2P)_2Cu(NC)_2BH_2$ have also been obtained, although the latter is air-sensitive and reacts instantly with an excess of phosphine to produce the monomeric $(MePh_2P)_3Cu(NC)_2BH_2$. Studies are being carried out not only to examine the potentially interesting physical and

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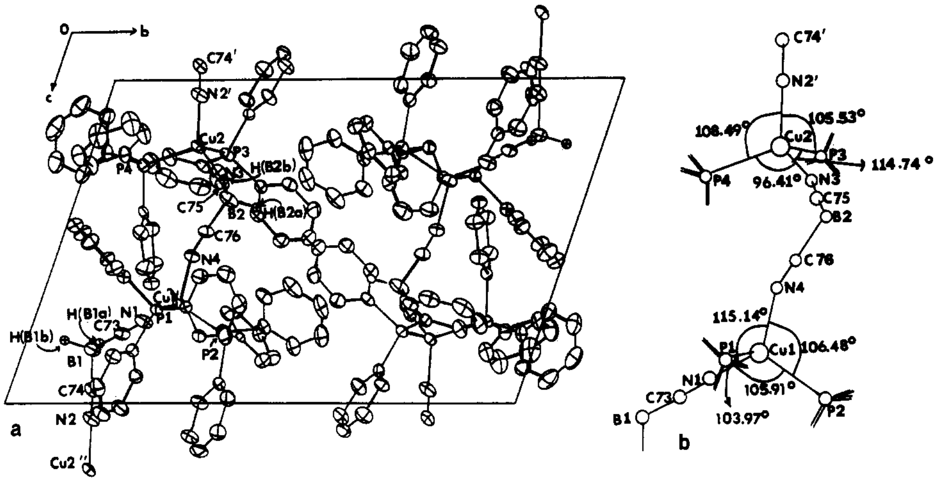

Figure 1. (a) Projection of the crystal structure of $[(PPh_3)_2Cu(NC)_2BH_2]_x$ along the *a* axis. Symmetry code: (′) $x, y, -1 + z$; (″) $x, y, 1 + z$. Principal bond lengths (Å) with their standard deviations in parentheses: Cu(1)–P(1), 2.264 (1); Cu(1)–P(2), 2.282 (1); Cu(1)–N(1), 2.023 (5); Cu(1)–N(4), 2.033 (4); Cu(2)–P(3), 2.266 (1); Cu(2)–P(4), 2.278 (2); Cu(2)–N(3), 2.059 (4); Cu(2)–N(2′), 2.006 (4); N(1)–C(73), 1.122 (7); N(2)–C(74), 1.127 (7); B(1)–C(73), 1.573 (9); B(1)–C(74), 1.575 (8); N(3)–C(75), 1.139 (6); N(4)–C(76), 1.140 (7); B(2)–C(75), 1.584 (8); B(2)–C(76), 1.583 (10); B(1)–H(Bla), 1.14 (4); B(1)–H(B1b), 1.06 (4); B(2)–H(B2a), 1.13 (5); B(2)–H(B2b), 1.02 (4). Principal bond angles (deg) with their standard deviations in parentheses: P(1)–Cu(1)–P(2), 116.86 (4); P(1)–Cu(1)–N(1), 103.97 (13); P(1)–Cu(1)–N(4), 115.14 (13); P(2)–Cu(1)–N(1), 105.91 (13); P(2)–Cu(1)–N(4), 106.48 (13); N(1)–Cu(1)–N(4), 107.76 (18); P(3)–Cu(2)–P(4), 124.36 (5); P(3)–Cu(2)–N(3), 114.74 (11); P(3)–Cu(2)–N(2′), 105.53 (13); P(4)–Cu(2)–N(3), 96.41 (12); P(4)–Cu(2)–N(2′), 108.49 (13); N(3)–Cu(2)–N(2′), 105.99 (16); Cu(1)–N(1)–C(73), 173.0 (5); Cu(2)–N(2′)–C(74′), 165.8 (4); B(1)–C(73)–N(1), 177.1 (6); B(1)–C(74)–N(2), 177.9 (6); C(73)–B(1)–C(74), 109.5 (5); Cu(2)–N(3)–C(75), 162.7 (4); Cu(1)–N(4)–C(76), 164.4 (4); B(2)–C(75)–N(3), 174.8 (5); B(2)–C(76)–N(4), 173.1 (6); C(75)–B(2)–C(76), 113.5 (5). (b) Projection along the *a* axis showing the polymer framework (structural details of the phenyl groups and boron hydrogen atoms omitted for clarity).

chemical properties of these systems but also to determine the properties of the phosphine necessary to stabilize the polymers.

Full details of the PPh_3 polymer and related complexes with various other phosphine ligands will appear in later publications.[8]

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Supplementary Material Available: Listings of crystal structure data, i.e., bond lengths and angles, atomic coordinates, and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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